

Theory of optical conductivity in doped manganites

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The frequency and temperature dependence of the optical conductivity of ferromagnetic manganites is explained within the framework of the bipolaron theory. As these materials are cooled below the Curie temperature, the colossal magnetoresistance (CMR) is accompanied by a massive transfer of the spectral weight of the optical conductivity to lower frequencies. As with the CMR itself, this change in the optical conductivity is explained by the dissociation of bipolarons into small polarons by exchange interaction with the localized Mn spins during the transition to the low temperature ferromagnetic phase.

71.30.+h, 71.38.+i, 72.20.Jv, 78.20.Bh

It is well established that carriers in manganites are strongly coupled with the lattice vibrations [1,2]. As we have recently shown [3] the interplay of the electron-phonon and exchange interactions results in a current carrier density collapse (CCDC) at the transition. Owing to the strong electron-phonon interaction, polaronic carriers are bound into almost immobile bipolarons in the paramagnetic phase. A few thermally excited non-degenerate polarons polarize localized Mn *d* electrons. As a result, the exchange interaction breaks bipolarons below T_c if the $p-d$ exchange energy $J_{pd}S$ of the polaronic carriers with the localized Mn *d* electrons is larger than the bipolaron binding energy Δ . Hence, the density of current carriers (polarons) suddenly increases below T_c , which explains the resistivity peak and CMR experimentally observed in many ferromagnetic oxides [4–6]. We have also shown [7] that CCDC explains the giant isotope effect [8], the tunneling gap [9], the specific heat anomaly [10], along with the temperature dependence of the dc resistivity [11].

Recent studies of the optical conductivity [12–15] and photoemission [16] unambiguously confirmed a non-metallic origin of the ferromagnetic phase. In particular, a broad incoherent spectral feature [12–15] in the midinfrared region and a pseudogap in the excitation spectrum [16] were observed, while the coherent Drude weight appeared to be *two orders* of magnitude smaller [13,14] than expected for a metal, or almost *absent* [15]. These and other studies [17] prove that carriers retain their polaronic character well below T_c , in agreement with our theory of CMR [3]. However, a conspicuous sudden spectral weight transfer with temperature [13–15] as well as a pronounced peak structure [15] in the optical conductivity below T_c remain to be understood.

In this Letter we propose a theory of the optical conductivity, including the *sudden spectral weight transfer* below the ferromagnetic transition, based on the idea of the current carrier density collapse. We show that the

high-temperature optical conductivity is well described by the small bipolaron absorption, while the low temperature midinfrared band is due to absorption by small polarons. The magnetic bipolaron breaking below T_c shifts the spectral weight from the bipolaronic peak to the polaronic one. We describe the optical spectra of the layered ferromagnetic ($T_c = 125\text{K}$) crystals $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ [15] in the entire frequency and temperature range, and show that the optical data provides a strong evidence for CCDC.

The optical intraband conductivity of a charge-transfer doped insulator with (bi)polaronic carriers is the sum of the polaron $\sigma_p(\nu)$ and bipolaron $\sigma_b(\nu)$ contributions at the given frequency ν . Their frequency dependences are described in the literature [18–20]. Both have almost a Gaussian shape given by

$$\sigma_{\text{intra}}(\nu) = \frac{\sigma_0 \mathcal{T}^2}{\nu} \left[\frac{n}{\gamma_p} \exp [-(\nu - \nu_p)^2 / \gamma_p^2] + \frac{x-n}{\gamma_b} \exp [-(\nu - \nu_b)^2 / \gamma_b^2] \right], \quad (1)$$

where $\sigma_0 = 2\pi^{1/2}e^2/a$ is a constant with a the lattice spacing, \mathcal{T} the hopping integral, n the (atomic) polaron density, and x the doping level. Here and further we take $\hbar = c = 1$.

Within the Holstein model with a local electron-phonon interaction, the polaron absorption has a maximum around $\nu_p = 2E_p$ [21–23], while the on-site bipolaron absorption has a maximum around $\nu_b = 4E_p - U$ [24]. Here E_p is the polaronic (Franck-Condon) shift of the electron level and U is the on-site (Hubbard) repulsion. The broadening of the absorption lines is due to the zero-point quantum fluctuations of ions, $\gamma_p = \gamma_b = (4E_p\omega)^{1/2}$, if the temperature is well below the characteristic phonon frequency ω . The spectral shape, Eq. (1), is applied in a wide frequency range, $\nu \gg \omega$, where the Franck-Condon principle applies (see, for example, [19]).

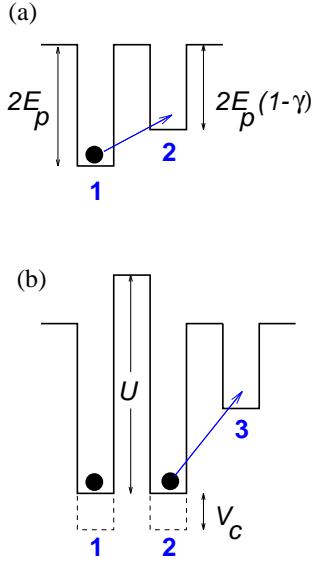


FIG. 1 Alexandrov and Bratkovsky

FIG. 1. Adiabatic energy levels for the small polaron (a) and the inter-site small bipolaron (b). For notations see text.

The Holstein model with on-site bipolarons is highly unrealistic because of a very large on-site Coulomb repulsion and the long-range (Fröhlich) electron-phonon interaction, which dominates in ionic solids. The latter is not reduced to a short-range interaction because heavy polarons cannot screen high-frequency crystal field oscillations in the low mobility solids. On the contrary, small polarons and small *intersite* bipolarons formed by the Fröhlich interaction together with the deformation potential are rather feasible [25,26]. Applying the Franck-Condon principle in the adiabatic regime, $\nu \gg \omega$, one can readily generalize the (bi)polaronic absorption, Eq. (1), to describe the optical conductivity of these quasi-particles, Fig. 1. The electron ‘sitting’ on a site “1”, Fig. 1(a), lowers its energy by an amount $2E_p$, with respect to an atomic level in the undeformed lattice, owing to the lattice deformation. If the electron-phonon interaction has a finite radius, the electron also creates some deformation around a neighboring site “2”, lowering its energy level by an amount $2E_p(1-\gamma)$, where [25]:

$$\gamma = \sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 [1 - \cos(\mathbf{q} \cdot \mathbf{a})] / \sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 \quad (2)$$

with \mathbf{a} the lattice vector connecting the neighboring sites. The coefficient γ strongly depends on the radius of the interaction. In the Holstein model with \mathbf{q} -independent electron-phonon coupling, $\gamma(\mathbf{q})$, this coefficient equals unity. Hence, there is no lattice deformation at the neighboring site. On the contrary, in the Fröhlich case, $\gamma(\mathbf{q}) \propto 1/q$, and the coefficient is quite small, $\gamma \approx 0.2 - 0.4$ [25] depending on the dimensionality

of the system and the unit cell geometry. In that case, there is a significant lowering of the neighboring energy level and, as a result, of the polaron mass [26]. Hence, generally, the peak energy in the polaron absorption is found at

$$\nu_p = 2\gamma E_p, \quad (3)$$

and the activation energy of the high-temperature dc-conductivity is $E_a = \gamma E_p/2$ [19]. One can apply the same ‘frozen lattice distortion’ arguments to the inter-site bipolaron absorption, Fig. 1b. The electron energy on a site “2” is $-2E_p - 2E_p(1-\gamma) + V_c$, where the first contribution is due to the lattice deformation created by the electron itself, while the second contribution is due to the lattice deformation around the site “2” created by the other electron of the pair on the site “1”, which is the polaron-polaron attraction [20]. After absorbing the quantum of radiation, the electron hops from site “2” to the empty site “3” into a state with the energy $-2E_p(1-\gamma)$, which corresponds to an absorption frequency

$$\nu_b = 2E_p - V_c, \quad (4)$$

where now V_c is the inter-site Coulomb repulsion. The quantum broadening of the polaronic and bipolaronic absorption is given by $\gamma_p = \gamma_b = (4\gamma E_p \omega)^{1/2}$. Since doped manganites are intrinsically disordered, their dielectric properties are inhomogeneous, and so is E_p , which fluctuates with a characteristic impurity broadening Γ_{im} . The convolution of the polaronic and bipolaronic absorption lines with the Gaussian distribution of E_p results in their having different linewidths, $\gamma_p = 2(\gamma E_p \omega + \gamma^2 \Gamma_{\text{im}}^2)^{1/2}$ and $\gamma_b = 2(\gamma E_p \omega + \Gamma_{\text{im}}^2)^{1/2}$ for polaronic and bipolaronic absorption, respectively. The Coulomb repulsion V_c can be readily estimated as $V_c = 2E_p - \nu_b$ from (4).

The total absorption is the sum of the intraband polaronic and bipolaronic terms, Eq. (1), and the interband absorption, $\sigma(\nu) = \sigma_{\text{intra}}(\nu) + \sigma_{\text{inter}}(\nu)$. In the layered compounds like $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, the intraband contribution to the out-of-plane conductivity is negligible [15]. Hence, one can take the c-axis optical conductivity $\sigma_c(\nu)$ as a measure of the interband contribution to the in-plane conductivity with a scaling factor, s , $\sigma_{\text{inter}}(\nu) \simeq s\sigma_c(\nu)$. The scaling factor s is the square of the ratio of the in-plane components of the dipole matrix element for the interband transitions to its z component (z is the out-of-plane direction). It can be readily determined by comparing the in-plane and out-of-plane optical conductivities at high frequencies, where intraband absorption is irrelevant. The result of the comparison of the present theory with the experiment [15] is shown in Fig. 2. At temperatures above the transition ($T = 130\text{K}$) the polaron density is very low owing to CCDC [3], so the intraband conductivity is due to bipolarons only,

$$\sigma(\nu) = \frac{\sigma_0 x T^2}{\nu \gamma_b} \exp [-(\nu - \nu_b)^2 / \gamma_b^2] + s\sigma_c(\nu). \quad (5)$$

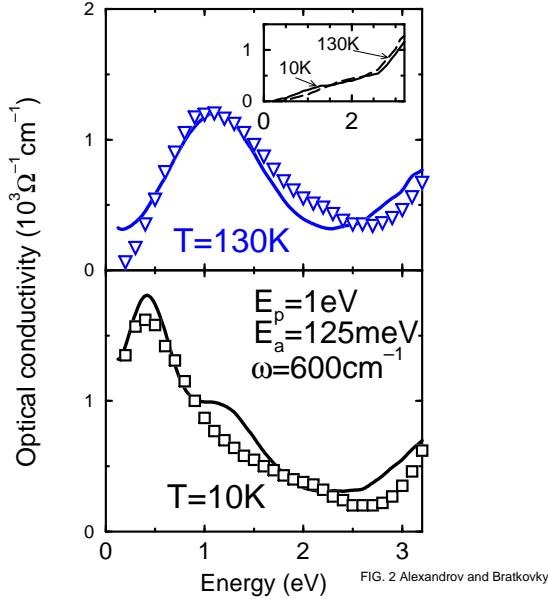


FIG. 2. Optical conductivity of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ [15] compared with the theory (solid line) above T_c (top panel) and well below T_c (bottom panel). Inset: c-axis optical conductivity.

This expression fits the experiment fairly well with $\nu_b = 1.24$ eV and $\gamma_b = 0.6$ eV, Fig. 2. The scaling factor is estimated as $s = 0.6$. When the temperature drops below T_c , at least some of the bipolarons break apart by the exchange interaction with Mn sites, because one of the spin-polarized polaron bands falls suddenly below the bipolaron level by an amount $(J_{pd}S - \Delta)/2$, Fig. 3 [3]. The intraband optical conductivity is determined now by both the polaronic and bipolaronic contributions, Eq. (1), and that explains the sudden spectral weight transfer from $\nu = \nu_b$ to $\nu = \nu_p$ observed below T_c in the ferromagnetic manganites [13–15]. The experimental spectral shape at $T = 10\text{K}$ is well described by Eq. (1) with $n = x/5$, $\nu_p = 0.5$ eV and $\gamma_p = 0.3$ eV (Fig. 2). With the use of the polaronic and bipolaronic linewidths we find $\gamma \simeq 0.25$ and $\Gamma_{\text{im}} \simeq 0.27\text{eV}$ by taking for the optical phonon frequency a value $\omega = 600\text{cm}^{-1}$ (i.e. $\simeq 74\text{meV}$), typical of oxides [26]. Then the polaron level shift is $E_p = 1.0\text{eV}$ (corresponding to the activation energy $E_a = 125\text{meV}$), and the Coulomb energy is $V_c = 0.76\text{eV}$ in agreement with estimates using the high-frequency and static dielectric constants [25], high-temperature dc hopping conductivity, phonon spectra, and the Coulomb law, respectively.

We do not expect any significant temperature dependence of the optical conductivity in the paramagnetic phase because the polaron density remains small compared with the bipolaron density above T_c [3]. The temperature dependence of the polaron density below T_c can be found from our Hartree-Fock equations [3] generalized for arbitrary temperatures

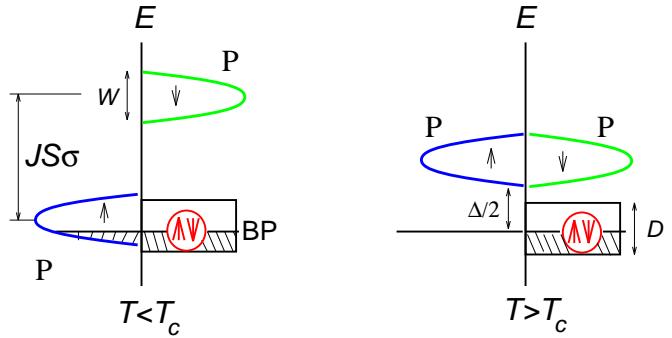


FIG. 3. Spin-polarized polaron band in the ferromagnetic phase ($T < T_c$) overlaps with the bipolaron (impurity) band, breaking up a fraction of the bipolarons.

$$n = \frac{t}{2w} \ln \left[\frac{1 + 2y \cosh(\sigma/t) + y^2}{1 + 2ye^{-2w/t} \cosh(\sigma/t) + y^2e^{-4w/t}} \right], \quad (6)$$

$$m = \frac{t}{2w} \ln \left[\frac{1 + 2ye^{-w/t} \cosh(\frac{\sigma+w}{t}) + y^2e^{-2w/t}}{1 + 2ye^{-w/t} \cosh(\frac{\sigma-w}{t}) + y^2e^{-2w/t}} \right], \quad (7)$$

$$\sigma = B_2[m/(2t)], \quad (8)$$

where now

$$y = e^{-\delta/t} \left[\frac{\sinh[(x-n)d/(2xt)]}{\sinh[(x+n)d/(2xt)]} \right]^{1/2}. \quad (9)$$

Here $B_S(z) = [1 + 1/(2S)] \coth[(S + 1/2)z] - [1/(2S)] \coth(z/2)$ is the Brillouin function, m and σ are the relative magnetization of polarons and of Mn, respectively. The reduced temperature is $t = 2k_B T/(J_{pd}S)$, and the dimensionless binding energy $\delta = \Delta/(J_{pd}S)$. Compared with a nondegenerate case [3] these equations take into account a finite polaron, $w = W/J_{pd}S$ and bipolaron, $d = D/J_{pd}S$, widths of the energy level distribution, essential at low temperatures, Fig. 3. We also assume here that immobile bipolarons are localized by the impurities and there is no more than one bipolaron in a single localized state ('single well-single particle' approximation [27]). Therefore, the total number of states in the bipolaron (impurity) band is x . Then the bipolaron density is determined by the integral $\int N_L(E) f_b(E) dE$, where $N_L(E) = x/D$ the density of bipolaron (*two-particle*) impurity states in the energy interval $-D/2 < E < D/2$, and $f_b(E) = [1 + y^{-2} \exp[(E - \Delta)/T]]^{-1}$ the bipolaron distribution function with the chemical potential $\mu \equiv T \ln y$. This integral should be equal to $(x-n)/2$, yielding the Eq. (9). The polaron density at zero temperature is obtained from Eq. (6) with $\sigma = 1$ as

$$n(T = 0) = \frac{2x(1 - \delta)}{d + 4xw}, \quad (10)$$

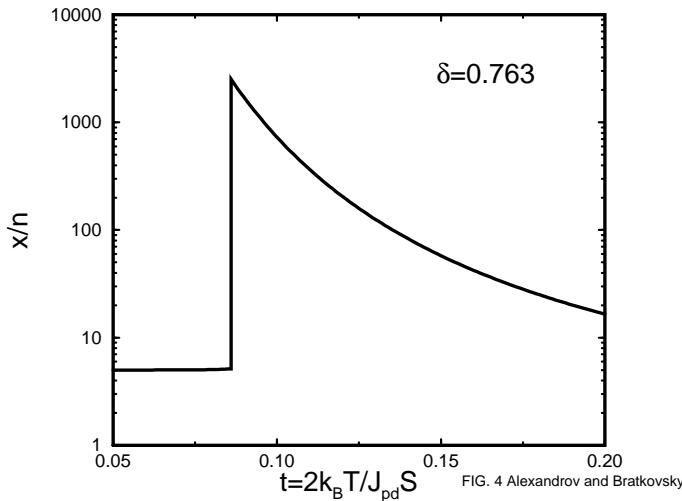


FIG. 4. Giant carrier density collapse in a charge transfer doped ferromagnetic insulator with $\delta \equiv \Delta/J_{pd}S = 0.763$, corresponding to the observed drop of dc resistivity below T_c [15].

while in the paramagnetic phase, where $\sigma = 0$ one obtains

$$n(T > T_c) = \frac{t}{w} \exp(-\delta/t) \quad (11)$$

for $t_c \leq t \ll 1$. As a result there is a giant drop of the polaron density at T_c , which exponentially depends on the bipolaron binding energy. Because polarons are not degenerate in the paramagnetic phase we can apply our nondegenerate equations [3] to determine t_c at a given value of δ . We have verified that the observed drop of the dc resistivity below T_c [15] is well reproduced by our equations with $\delta = 0.763$ (Fig. 4). The giant drop of the polaron density from $x/5$ below T_c to the value 500 times smaller above T_c is obtained with the polaron bandwidth $w \simeq 0.15$ and with the width of the bipolaron impurity states $d \simeq 2.25$ (for $x = 0.2$).

In conclusion, we have developed the theory of the optical conductivity in doped magnetic charge-transfer insulators with a strong electron-phonon interaction. We have found that the spectral and temperature features of the optical conductivity of ferromagnetic manganites are well described by the bipolaron absorption in the paramagnetic phase and by the small polaron absorption in the ferromagnetic phase. The pair breaking by exchange interaction with the localized Mn spins explains the sudden spectral weight transfer in the optical conductivity below T_c . We argue that the optical probe of the incoherent charge dynamics in manganites provides another strong evidence for the carrier density collapse which we proposed earlier as the explanation of CMR.

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